

Essential Principles
of
ORGANIC CHEMISTRY

By
JAMES CASON

Professor of Chemistry
University of California at Berkeley

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CHAPTER 4

Alcohols as a Class of Organic Compounds

Alcohols are among the more important classes of organic compounds and are especially important as basic raw materials in the chemical industry. As has been mentioned in Chapter 2, a *class* of compounds is characterized by a common functional group. In the case of alcohols, this is the hydroxyl group, —OH . Since alcohols consist of the hydroxyl group attached to an alkyl radical, the *general formula* for alcohols is $\text{C}_n\text{H}_{2n+1}\text{OH}$. Since n may have any value, an infinite number of alcohols is theoretically possible, and thousands are actually known to chemists. Certain characteristics of ten of the more simple alcohols are listed in Table 1. In this table, each alcohol is named by placing the name of the alkyl radical as a separate word preceding the term alcohol. *Since the radical names are basic units in organic nomenclature, they should be learned.* It will be noted that each radical name except the first two carries a hyphenated, italicized " n " as prefix. This stands for "normal," and is read not as " n " but as "normal." It means that the carbon atoms in this alkyl radical are attached to each other in a linear fashion, with no branches

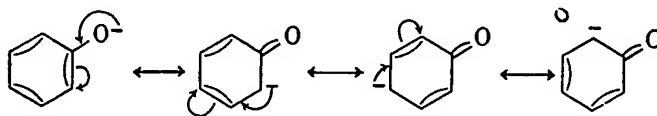
Table 1. Characteristics of Certain Alcohols

Name	Formula	Boiling point	Increment in B.P.	Melting point	Increment in M.P.
Methyl alcohol	$\text{CH}_3\text{—OH}$	64°			
Ethyl alcohol	$\text{CH}_3\text{—CH}_2\text{—OH}$	78°	14°		
<i>n</i> -Propyl alcohol	$\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—OH}$	98°	20°	−127°	37°
<i>n</i> -Butyl alcohol	$\text{CH}_3\text{—(CH}_2)_3\text{—OH}$	118°	20°	−90°	11°
<i>n</i> -Amyl alcohol	$\text{CH}_3\text{—(CH}_2)_4\text{—OH}$	138°	19°	−79°	28°
<i>n</i> -Hexyl alcohol	$\text{CH}_3\text{—(CH}_2)_5\text{—OH}$	157°	19°	−51°	17°
<i>n</i> -Heptyl alcohol	$\text{CH}_3\text{—(CH}_2)_6\text{—OH}$	176°	19°	−34°	18°
<i>n</i> -Octyl alcohol	$\text{CH}_3\text{—(CH}_2)_7\text{—OH}$	195°	20°	−16°	11°
<i>n</i> -Nonyl alcohol	$\text{CH}_3\text{—(CH}_2)_8\text{—OH}$	215°	18°	−5°	11.5°
<i>n</i> -Decyl alcohol	$\text{CH}_3\text{—(CH}_2)_9\text{—OH}$	233°		+6.5°	

They may be readily isolated from oil of cloves and oil of cayenne, respectively. The natural hormone, epinephrine, is a phenol with an amino group in the side chain.

Acidity of Phenols

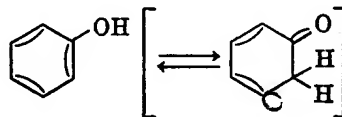
The phenols are weakly acidic compounds, in contrast with the alcohols which do not ionize in water solution. This difference may be anticipated, for the phenolate anion is stabilized by resonance, as shown in the following formulas:



The phenols are very weakly acidic, less so than carbonic acid, unless electron-withdrawing groups are substituted in the *ortho* or *para* positions. Just as electron withdrawal reduces the basic strength of amines (Chap. 24), it increases the acidic strength of phenols, and this is not a small effect. 2,4,6-Trinitrophenol (picric acid) is a stronger acid than phenol by a factor of one million.

The weakly acidic nature of most phenols may be turned to good advantage for their separation from neutral material and also carboxylic acids. Since both phenols and carboxylic acids occur rather widely in complex mixtures in nature, their separation is of particular significance. If a solution of organic compounds is extracted with an aqueous solution of strong alkali (sodium or potassium hydroxide), both phenols and carboxylic acids form salts which dissolve in the alkali. If carbon dioxide is passed into the alkaline solution, the phenols (weaker acids than carbonic acid) are freed from their salts while the carboxylic acids remain as their soluble salts. After separation of the phenols, the carboxylic acids can then be freed from their salts by addition of a strong acid such as sulfuric acid.

It should be noted that a phenol may be regarded as the enol form of a ketone:



Whereas most ketones exist almost entirely in the keto form (cf. Chap. 14), most phenols appear to be entirely in the enol form, for they do not give reactions of the carbonyl group. This seems a reasonable circumstance, for the resonance stabilization of benzene is lost in the keto form. The